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Region of Formation of Iron(III) Hydrogen Orthophosphate and Structural Changes in Humid Atmospheres

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The conditions of formation of the A and B forms of $Fe(H_2PO_4)_3$ by the reaction of Fe_2O_3 and H_3PO_4 have been established, and the thermal changes and structural changes in humid atmospheres investigated. 1) The A and B forms of $Fe(H_2PO_4)_3$ were readily formed by secondary heat treatment at 150 °C and 125 °C, respectively. 2) The forms of $Fe(H_2PO_4)_3$ were largely dependent on the heating rate in the primary heat treatment, *i.e.*, at a mean heating rate less than 7 °C/min the A form predominated, whereas above 60 °C/min the B form predominated. A heating rate between 7 and 60 °C/min gave a mixture of the A and B forms. 3) A close relationship between the water content of the primary product and yields of the A and B forms of $Fe(H_2PO_4)_3$ was found, *i.e.*, only the B form was obtained when the water content of the primary product was less than 7%, while the A form was readily formed when the water content was greater than 11%. 4) Heating the primary product under various degrees of humidity enabled the formation of $Fe(H_2PO_4)_3$ to be investigated. The effect of heating atmosphere was small except under vacuum. 5) The structural changes of the A and B forms of $Fe(H_2PO_4)_3$ under several humid atmospheres are summarized as follows:

$$\mathrm{Fe(H_2PO_4)_3\ B\ form} \xrightleftharpoons[\mathrm{P_2O_5}]{\text{air}} \mathrm{FeH_6(PO_4)_3} \xrightleftharpoons[\mathrm{P_2O_5}]{\text{wet air}} \text{amorphous}$$

$$\text{iron phosphate} \xrightarrow{\text{air}} \mathrm{FeH_3(PO_4)_2{\cdot}2.5H_2O}$$

$$\begin{tikzcd}
 & \mathrm{Fe(H_2PO_4)_3\ B\ form} \arrow[d, shift left, "\mathrm{P_2O_5}"] & \\
\mathrm{Fe(H_2PO_4)_3\ A\ form} \arrow[r, "\text{air}"] & \mathrm{FeH_6(PO_4)_3} \arrow[u, shift left, "\text{air}"] \arrow[r, shift left, "\text{wet air}"] & \text{amorphous} \arrow[l, shift left, "\mathrm{SiO_2}"]
\end{tikzcd}$$

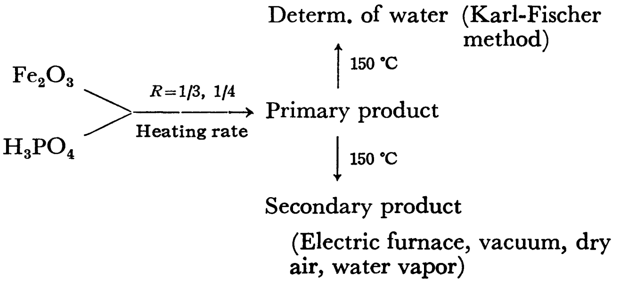
$$\text{iron phosphate} \xrightarrow{\text{air}} \mathrm{FeH_3(PO_4)_2{\cdot}2.5H_2O}$$

Iron phosphates have been studied for several years and already in 1878 several iron phosphates had been synthesized by Erlenmeyer.[1)] Since then the structural chemistry of several natural iron phosphates, such as strengite $FePO_4{\cdot}2H_2O$,[2)] vivianite $Fe_3(PO_4)_2{\cdot}8H_2O$,[3)] ludlamite $Fe_3(PO_4)_2{\cdot}4H_2O$[4)] and the like,[5—7)] have been conducted by many researchers. Carter,[8)] Jameson[9)] and Kobayashi[10)] have studied the phase diagram of the Fe_2O_3–P_2O_5–H_2O system at 25 °C and several iron phosphates synthesized. d'Yvoire[11)] has studied in detail the similarity of structure between iron phosphate and aluminum phosphate.

Recently, fundamental studies of iron phosphate as an inorganic ion exchanger have been published,[10,12—14)] but a systematic study of the preparation of iron phosphates remains absent. Consequently it is difficult to obtain iron phosphates with fine reproducibility. In the present study, the authors investigated the preparative methods for the A and B forms of iron hydrogen orthophosphate $Fe(H_2PO_4)_3$, and established the preparative conditions in the reaction of Fe_2O_3 and H_3PO_4. The thermal changes of the A and B forms of $Fe(H_2PO_4)_3$ as well as the structural changes under several different humid atmospheres were also investigated.

Experimental

Preparation of Iron Phosphate. Ferric oxide Fe_2O_3 (E. Merck) and 85% orthophosphoric acid were mixed in a gold or porcelain crucible in molar ratios Fe_2O_3/P_2O_5 (R) of 1/3 and 1/4. The mixture was heated at various heating rates by a weak flame with vigorous agitation to obtain a grey, highly viscous product. (This is designated as the primary heat treatment, giving the primary products.) A small amount (0.5—0.6 g) of the primary product was accurately weighed, and the water content determined by the Karl-Fischer method at 150 °C. Another portion was heated at 150 °C for 5 h in a thermostated electric furnace, under vacuum (0.01 mmHg), in dry air (50 ml/min, vapor pressure 0—1 mmHg), and in water vapor (500 g H_2O/h, vapor pressure 760 mmHg). (This is designated as the secondary heat treatment, giving the secondary products.) The experimental method may be shown schematically as follows:



The temperature of the primary heat treatment is affected by the amount of starting material, the molar ratio R and the heating rate; the temperature being generally approximately 70—170 °C.

The iron phosphates prepared at 150 °C were relatively hard, but absorbed moisture on standing in air. Thus, X-ray analysis, differential thermal analysis (DTA), and thermogravimetry (TG) of iron phosphates were conducted immediately after preparation.

Apparatus and Methods. The X-ray analysis was conducted with a Rigaku Denki Geigerflex X-ray diffractometer, using Ni filtered Cu $K\alpha$ radiation. A Kyoto Denshi Karl-Fischer Titrator was used for the determination of water. A Rigaku Denki Differential Thermogravimetric Analyzer, 8076E1, was used for the DTA and TG. The X-ray analysis, differential thermal analysis, and thermogravimetry of iron phosphates were conducted by the methods described in a previous paper.[15)]

The yields of the A and B forms of $Fe(H_2PO_4)_3$, $FeHP_2O_7$, $Fe_4(P_2O_7)_3$ and $FeH_6(PO_4)_3$ were determined from the integrated intensities of the characteristic X-ray diffraction peaks; *i.e.*, type A of $Fe(H_2PO_4)_3$ by the peak at d=3.634 Å; type B of $Fe(H_2PO_4)_3$, by that at 7.724 Å; $FeHP_2O_7$, by that at 3.860 Å; $Fe_4(P_2O_7)_3$, by that at 5.336 Å; and $FeH_6(PO_4)_3$, by that at 8.776 Å.

Results and Discussion

Relationship between Yields of Iron(III) Phosphates and Heating Temperature. Figure 1 shows the relationship between the heating temperature and the yields of iron phosphates in the reaction of Fe_2O_3 and H_3PO_4 at a molar ratio P_2O_5/Fe_2O_3 ($1/R$) of 3. As seen, the crystalline iron phosphates formed at temperature below 250 °C were four, namely, the A and B forms of $Fe(H_2PO_4)_3$, $FeHP_2O_7$, and $Fe_4(P_2O_7)_3$. At temperatures below 200 °C, iron hydrogen orthophosphate predominated, whereas above 225 °C pyrophosphate predominated. The A form of $Fe(H_2PO_4)_3$ was formed at temperatures below 200 °C, and especially at 150 °C. The B form was formed at temperatures below 175 °C, particularly readily at 125 °C. At temperatures above 225 °C $FeHP_2O_7$ and $Fe_4(P_2O_7)_3$ were obtained in a mixture, but in the temperature range 200—250 °C, the presence of large quantity of amorphous iron phosphate was proved by X-ray diffraction. The poor yields of $FeHP_2O_7$ and $Fe_4(P_2O_7)_3$ may be explained in terms of the mixing rate (R) of phosphoric acid and Fe_2O_3. $R=1/3$ corresponds to the meta-composition, and the quantity of phosphoric acid is too large to form iron pyrophosphate. No distinct difference could be established between the temperature of formation of $FeHP_2O_7$ and that of $Fe_4(P_2O_7)_3$, while considerable difference was observed between the temperature of formation of the A form of $Fe(H_2PO_4)_3$ and that of the B form. This establishes that the B form is prefered at low temperatures. At 150 °C, however, both forms were obtained in a mixture, and the reproducibility of yield was poor. It was also discovered that the yields were affected not only by the heating temperature but also by the conditions of the primary heat treatment. Maintaining the molar ratios and the temperatures of the primary and secondary heat treatments did not always give the same form of $Fe(H_2PO_4)_3$. Thus, the primary heat treatment, heating rate, the state of the primary product, the water content and heating atmosphere in the secondary heat treatment were further investigated. With molar ratios $1/R$ of 4 and 3, almost the same results were obtained. At a secondary heat treatment temperature below 110 °C, the product did not solidify and crystalline iron phosphate could not be obtained.

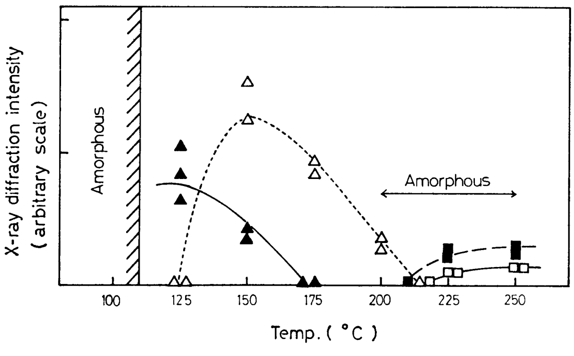


Fig. 1. Relationship between heating temperature and the yields of iron phosphates at $P_2O_5/Fe_2O_3=3$.
-△-: $Fe(H_2PO_4)_3$(A), -▲-: $Fe(H_2PO_4)_3$(B),
-■-: $FeHP_2O_7$, -□-: $Fe_4(P_2O_7)_3$.

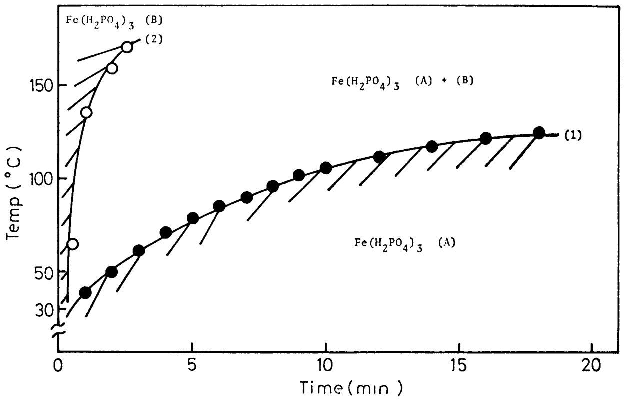


Fig. 2. Relationship between the formation of $Fe(H_2PO_4)_3$ (A), (B) and heating rate in the primary heat treatment. Molar ratio (P_2O_5/Fe_2O_3);3, heating rate; (1): 7 °C/min, (2): 60 °C/min, secondary heat treatment; 150 °C, 5 h.

Relationship between the Formation of the A and B Forms of $Fe(H_2PO_4)_3$ and the Heating Rate. Figure 2 illustrates the change in formation of the A and B forms of $Fe(H_2PO_4)_3$ with changes in the heating rate in the primary heat treatment. As shown by curve (1) in Fig. 2, slow heating at a mean heating rate less than 7 °C/min results in the exclusive formation of the A form. As can be seen from curve (2), rapid heating at a rate in excess of 60 °C/min produces exclusively the B form. Heating at a rate between 7 and 60 °C/min (the region surrounded by curves (1) and (2) in Fig. 2) results in a mixture. The A form, however, predominates at a lower heating rate (10—20 °C/min), whereas the B form predominates at a higher heating rate (40—60 °C/min). The above results were highly reproducible, there being only a few exceptions in 80 experiments. These results are only applicable for highly viscous primary products. Further heating of the viscous primary product and subsequent solidification in the course of the primary heat treatment, however, gave a different relationship, the results of which are shown in Fig. 3. At a primary heat treatment of heating rate below 2.5 °C/min (curve (1) in

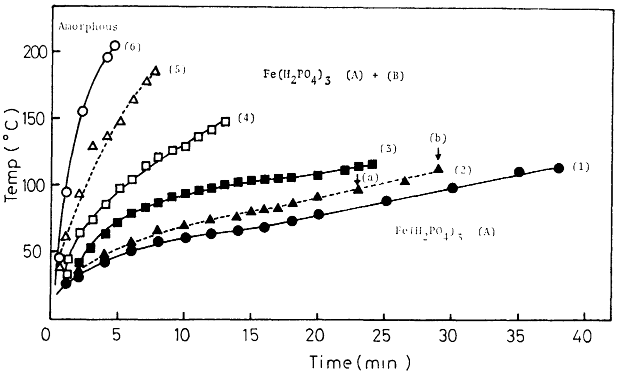


Fig. 3. Relationship between the formation of Fe-$(H_2PO_4)_3$ (A), (B) and heating rate in the primary heat treatment. Molar ratio (P_2O_5/Fe_2O_3): 3, secondary heat treatment: 150 °C, 5 h, heating rate; (1): 2.5 °C/min, (2): 3.7 °C/min, (3): 4.2 °C/min, (4): 9.6 °C/min, (5): 21.7 °C/min, (6): 40.2 °C/min.

Fig. 3), only the A form of $Fe(H_2PO_4)_3$ was obtained. At a primary heat treatment of heating rate above 40 °C/min (curve (6)), no crystalline iron phosphate was formed. At a primary heat treatment of heating rate of 3—40 °C/min (curves (2)—(5)), a mixture of the A and B forms was produced. Thus, only the B form of $Fe(H_2PO_4)_3$ could not be obtained from the solidified primary products. Two samples of the primary product obtained at a mean heating rate of about 3.7 °C/min (curve (2)), one of which was a highly viscous nature corresponding to point (a) and other the solidified state corresponding to point (b), were submitted for secondary heat treatment at 150 °C for 5 h. The iron phosphate formed from the former was the A form of $Fe(H_2PO_4)_3$, while that from the latter was a mixture of both A and B forms. The amounts of water liberated on heating the primary products corresponding to points (a) and (b) at 150 °C were 13.5% and 9.4%, respectively, indicating that since the primary product of the solidified state which was subjected to primary heat treatment at a higher temperature than that of the highly viscous state, the water content of the latter, corresponding to point (a), may be more than that of the former, corresponding to point (b). Based on this, it may be seen that the formation of both forms is strongly dependent on the state of the primary products, *i.e.*, at the same heating rate, the formation regions of the A and B forms for the highly viscous primary products differ from those for the solidified primary products. Furthermore, as can be seen from Figs. 2 and 3, the formation region of the mixture of both forms in the solidified primary product is greater than that in the highly viscous primary product.

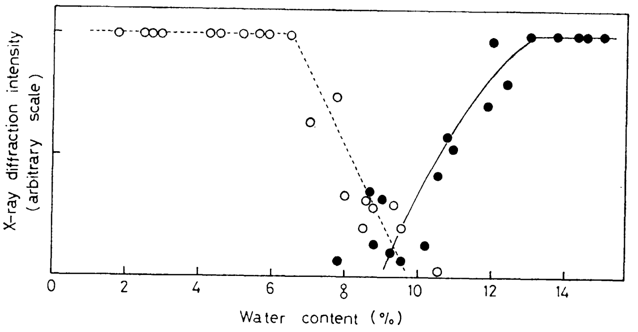


Fig. 4. Relationship between water content of the primary product and the yields of the A and B types of Fe-$(H_2PO_4)_3$.
-●-: $Fe(H_2PO_4)_3$ A type, --○--: $Fe(H_2PO)_3$ B type, Molar ratio (P_2O_5/Fe_2O_3): 3, secondary heat treatment: 150 °C, 5 h.

Relationship between Water Content of the Primary Product and Yields of Iron(III) Hydrogen Orthophosphate. As described above, the formation of the A and B forms of $Fe(H_2PO_4)_3$ strongly depend on the heating temperature, heating rate and the state of the primary product. Thus, the relationship between the water content of the primary product and yields of the A and B forms of $Fe(H_2PO_4)_3$ was investigated, the results of which are shown in Fig. 4. From a primary product containing approximately 7% or less of water, only the B form of $Fe(H_2PO_4)_3$ was obtained, while from a primary product containing 11% or more of water, only the A form was obtained. From primary products having between 7.5 and 10.5% water content, a mixture of both A and B forms was obtained. The results of DTA and TG of the primary products suggest that the water liberated on heating the primary product at 150 °C may be water loosely bound on the solid surface, and not the structural water (P–OH) of iron phosphate. It is evident, therefore, that the water content (loosely bound water) of the primary product strongly affects the formation of the A and B forms of $Fe(H_2PO_4)_3$. It was also estab-

TABLE 1. FORMATION OF IRON PHOSPHATES AT A MOLAR RATIO (Fe_2O_3/P_2O_5) OF 1/3 UNDER VARIOUS HEATING ATMOSPHERES AT 150 °C

Heating rate (°C/min)	Water content (%)	Electric furnace	Water vapor	Dry air	Vacuum
2.4	12.7	A(s)	A(m)	A(m)	A(s)
6.6	11.7	A(vs)	A(vs)	A(vs)	A(vs)
17.9	10.2	A(w) B(vs)	A(w) B(m)	A(vw) B(m)	A(w)
55.6	5.8	A(w) B(vs)	A(vw) B(m)	A(vw) B(w)	Amorphous
62.2	4.4	B(vs)	B(vs)	B(s)	Amorphous
87.2	2.5	B(vs)	B(m)	B(w)	Amorphous

X-Ray diffraction intensity, vs: very strong, s: strong, m: medium, w: weak, vw: very weak.
Product, A: $Fe(H_2PO_4)_3$ A form, B: $Fe(H_2PO_4)_3$ B form.

lished that the water content was inversely proportional to the heating rate of the primary heat treatment, *i.e.*, the water content decreased with increase in the heating rate.

In conclusion the A form of $Fe(H_2PO_4)_3$ is formed more readily at a low rate of heating, namely in the region in which the water content of the primary product was high. The B form is prefered at a higher heating rate, *i.e.*, at lower water content of the primary product.

Formation of Iron(III) Phosphates in Several Heating Atmospheres. The primary products prepared by the above-mentioned methods at various heating rates, *i.e.*, primary products containing various water contents were heated at 150 °C for 5 h in various water vapor pressures and the formation of iron phosphate investigated. The results are summarized in Table 1. As can be seen from Table 1, the formation of iron hydrogen orthophosphate is only slightly dependent on the heating atmosphere, but strongly affected by the heating rate of the primary heat treatment and consequently, by the water content of the primary product. This strongly supports the relationship reported above between the water content of the primary product and yields of the A and B forms of $Fe(H_2PO_4)_3$, *i.e.*, at a low heating rate the A form predominates, while at a high heating rate, the B form predominates. In vacuum, the formation of the B form of $Fe(H_2PO_4)_3$ was not observed, amorphous iron phosphate being obtained at low water content.

DTA and TG of the A and B Forms of $Fe(H_2PO_4)_3$. Figure 5 illustrates the results of DTA and TG for the A and B forms of $Fe(H_2PO_4)_3$. For the A form, endothermic peaks were observed at approximately 75—80, 250, and 475 °C. The products corresponding to each point, a (200 °C), b (250 °C), c (300 °C), d (400 °C), e (500 °C), and f (700 °C) on the DTA curve were investigated by powder X-ray diffraction. At point a, only the starting material, the A form of $Fe(H_2PO_4)_3$ was observed. Thus, the small endothermic peak at approximately 75—80 °C, which is accompanied by a slight weight loss (0.9—1.2%), may be attributed to the removal of water adhering to the solid surface, namely adhesive water. Furthermore, from the X-ray diffraction patterns of the products corresponding to points b and c, it was shown that the A form of $Fe(H_2PO_4)_3$ is transformed into amorphous iron phosphate through the strong endothermic reaction with a weight loss caused by dehydration at about 250 °C. At point d, the amorphous iron phosphate was partially transformed into the B and C forms of $Fe(PO_3)_3$. Furthermore, the endothermic reaction at approximately 475 °C (point e), the amorphous iron phosphate was completely transformed into the C form of $Fe(PO_3)_3$, which did not change at 700 °C (point f). The results of the DTA and TG of the B form of $Fe(H_2PO_4)_3$ were almost identical with those of the A form. For the B form of $Fe(H_2PO_4)_3$, a small endothermic peak, accompanied by a 0.5—0.8% weight loss, was observed at approximately 75—80 °C. This weak endothermic reaction may be considered as the removal of adhesive moisture, since the X-ray diffraction patterns of the products at points g (120 °C) and h (200 °C), the B form of $Fe(H_2PO_4)_3$ did not change due to this endothermic reaction. Furthermore, a large endothermic peak with an accompanying weight loss was observed at 250 °C. In this endothermic reaction, the B form of $Fe(H_2PO_4)_3$ was dehydrated and transformed into amorphous iron phosphate, as shown by the X-ray diffraction patterns of the product corresponding to point i (300 °C). At point j (450 °C), the amorphous iron phosphate was partially transformed into a mixture of the A, B, and C forms of $Fe(PO_3)_3$. At approximately 500 °C, and endothermic peak with a weight loss due to dehydration of structural water (P–OH) was observed. It was shown by the X-ray diffraction pattern of the product corresponding to point k (520 °C) that in this endothermic reaction, the amorphous iron phosphate was completely transformed into a mixture of the A, B, and C forms of $Fe(PO_3)_3$. In the temperature range from 520 to 700 °C, no changes were observed on the DTA curve, but the X-ray diffraction pattern of the product corresponding to point l (700

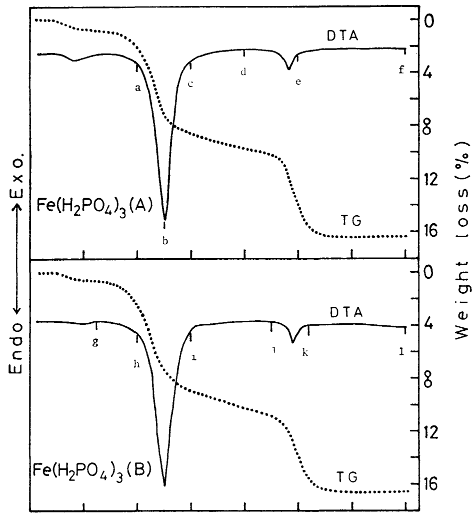


Fig. 5. DTA and TG of $Fe(H_2PO_4)_3$ (A), (B).
Sample; 20—22 mg, heating rate; 10 °C/min.

Table 2. Thermal changes of the A form of $Fe(H_2PO_4)_3$ in various heating atmospheres

Temp (°C)	Electric furnace	Water vapor	Vacuum
200	$Fe(H_2PO_4)_3$ A(s)	$FeHP_2O_7$(vw)	Amorphous
250	Amorphous	$FeHP_2O_7$(m)	Amorphous
300	Amorphous	$FeHP_2O_7$(m)	$Fe(PO_3)_3$ B(m), C(vs)
400	$Fe(PO_3)_3$ B(w), C(vs)	$Fe(PO_3)_3$ A(m), C(vs)	$Fe(PO_3)_3$ A(m), B(w), C(s)
500	$Fe(PO_3)_3$ C(vs)	$Fe(PO_3)_3$ C(vs)	$Fe(PO_3)_3$ A(w), C(vs)
700	$Fe(PO_3)_3$ C(vs)	$FePO_4$(vs)	$Fe(PO_3)_3$ C(vs)

X-Ray diffraction intensity, vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

TABLE 3. THERMAL CHANGES OF THE B FORM OF $Fe(H_2PO_4)_3$ IN VARIOUS HEATING ATMOSPHERES

Temp (°C)	Electric furnace	Water vapor	Vacuum
120	$Fe(H_2PO_4)_3$ B(vs)	$FePO_4\cdot 2H_2O$(m)	$Fe(H_2PO_4)_3$ B(m)
200	$Fe(H_2PO_4)_3$ B(m)	$FeHP_2O_7$(m)	Amorphous
300	Amorphous	$FeHP_2O_7$(s)	$Fe(PO_3)_3$ A(m), B(vs)
450	$Fe(PO_3)_3$ A(m), B(m), C(s)	$Fe(PO_3)_3$ A(w), C(vs)	$Fe(PO_3)_3$ A(m), B(s), C(m)
520	$Fe(PO_3)_3$ A(m), B(m), C(s)	$Fe(PO_3)_3$ C(vs)	$Fe(PO_3)_3$ A(w), C(vs)
700	$Fe(PO_3)_3$ C(vs)	$Fe_4(P_2O_7)_3$(vs) $FePO_4$(vs)	$Fe(PO_3)_3$ A(w), C(vs)

X-Ray diffraction intensity, vs: very strong, s: strong, m: medium, w: weak.

°C) showed that both the A and B forms of $Fe(PO_3)_3$ had already transformed into the C form of $Fe(PO_3)_3$.

The thermal changes of $Fe(H_2PO_4)_3$ at temperatures corresponding to points a—l on the DTA curves of the A and B forms of $Fe(H_2PO_4)_3$ were also investigated, the results of which are summarized in Tables 2 and 3. In all experiments, the samples were heated for 5 h. The results of the thermal changes of the A and B forms of $Fe(H_2PO_4)_3$ in an electric furnace largely support the results of the DTA study described above. The results of the thermal changes of both A and B forms in an atmosphere of water vapor differ considerably from those in other heating atmospheres, *i.e.*, in an atmosphere of water vapor below 300 °C, the A form of $Fe(H_2PO_4)_3$ gives $FeHP_2O_7$ and is transformed into $Fe(PO_3)_3$ at 400 °C. At a temperature above 700 °C, $Fe(PO_3)_3$, liberating white P_2O_5 fumes, decomposes to form $FePO_4$. The formation of $FePO_4$ may be interpreted in terms of evaporation of the P_2O_5 component caused by the flow of water vapor at high temperature. Under vacuum, both A and B forms of $Fe(H_2PO_4)_3$ begin to transform into amorphous iron phosphate at 200 °C. This transformation temperature is approximately 50—100 °C lower than in the electric furnace. Under vacuum, furthermore, the formation of $Fe(PO_3)_3$ was observed at 300 °C. Thus, it may be concluded that the thermal changes shift to lower temperatures under vacuum.

From the above experimental results, the thermal changes in air of the A and B forms of $Fe(H_2PO_4)_3$ may be given by:

$$Fe(H_2PO_4)_3\ \text{A form} \xrightarrow{250\,^{\circ}\mathrm{C}} \text{amorphous iron phosphate}$$
$$\xrightarrow{400\,^{\circ}\mathrm{C}} Fe(PO_3)_3\ \text{B + C form} \xrightarrow{500\,^{\circ}\mathrm{C}} Fe(PO_3)_3\ \text{C form}$$
$$Fe(H_2PO_4)_3\ \text{B form} \xrightarrow{250\,^{\circ}\mathrm{C}} \text{amorphous iron phosphate}$$
$$\xrightarrow{450\,^{\circ}\mathrm{C}} Fe(PO_3)_3\ \text{A+B+C form} \xrightarrow{700\,^{\circ}\mathrm{C}} Fe(PO_3)_3\ \text{C form}$$

Changes of the A and B Forms of $Fe(H_2PO_4)_3$ in Various Humid Atmospheres. The structural changes of the A and B forms of $Fe(H_2PO_4)_3$ after standing in various humid atmospheres are shown in Figs. 6a—6c. As may be seen from Fig. 6a, the B form of $Fe(H_2PO_4)_3$ was completely transformed into $FeH_6(PO_4)_3$, on standing in air for 4 days. The X-ray diffraction pattern of the product was in fair agreement with that of $FeH_6(PO_4)_3$ already reported by Kobayashi.[10] The compound $FeH_6(PO_4)_3$ obtained under the above conditions, on standing in a desiccator with P_2O_5, was transformed into the B form of $Fe(H_2PO_4)_3$ starting from the third day. The amount of $FeH_6(PO_4)_3$ gradually decreases with time, virtually disappearing on the seventh day. Thus, the B form of $Fe(H_2PO_4)_3$, on standing in air, absorbs moisture to form $FeH_6(PO_4)_3$, but the latter is dehydrated in a desiccator with P_2O_5, reverting to the former again. As may be seen from Fig. 6b, on standing in wet air (water vapor 20—25 mmHg) for 2 h, the B form is completely transformed into amorphous iron phosphate. This amorphous iron phosphate is transformed into $FeH_6(PO_4)_3$ on standing in a desiccator with P_2O_5 for 24 h. On standing in a desiccator with P_2O_5 for more than 7 days, $FeH_6(PO_4)_3$ is further dehydrated to give the B form of $Fe(H_2PO_4)_3$. This suggests that the changes of the B form of $Fe(H_2PO_4)_3$ into $FeH_6(PO_4)_3$ and amorphous iron phosphate caused by moisture absorption may be reversible. The A form of

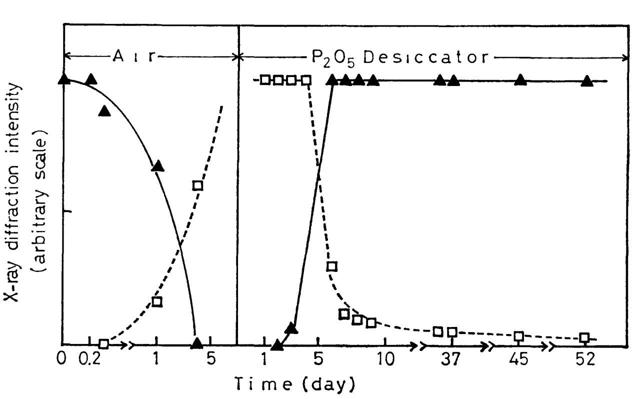


Fig. 6a. Structural change of iron phosphate in various humid atmospheres.
—▲—: $Fe(H_2PO_4)_3$(B), ···□···: $FeH_6(PO_4)_3$.

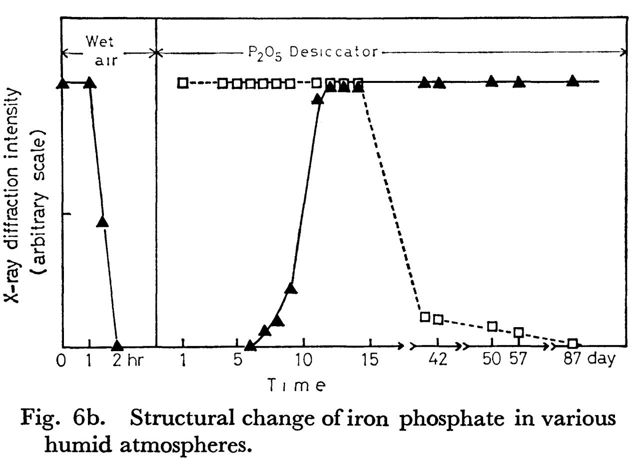


Fig. 6b. Structural change of iron phosphate in various humid atmospheres.
—▲—: $Fe(H_2PO_4)_3$(B), ···□···: $FeH_6(PO_4)_3$.

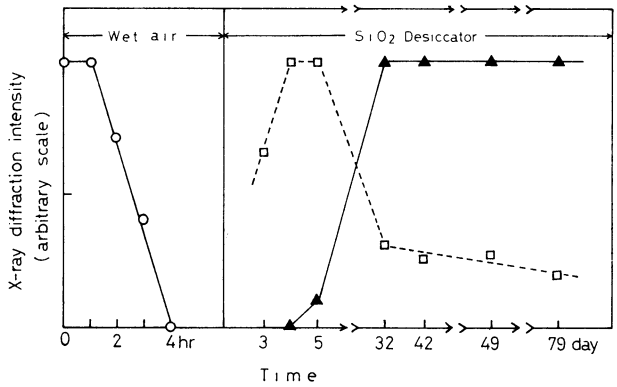


Fig. 6c. Structural change of iron phosphate in various humid atmospheres.
—○—: $Fe(H_2PO_4)_3$ (A), --▲--: $Fe(H_2PO_4)_3$ (B), —□—: $FeH_6(PO_4)_3$.

$Fe(H_2PO_4)_3$, as seen from Fig. 6c, is rapidly transformed into amorphous phosphate on standing in wet air, a result similar to that for the B form. Amorphous iron phosphate, on standing in a desiccator with silica gel, is transformed into $FeH_6(PO_4)_3$, which, beginning on the fifth day, is gradually transformed into the B form of $Fe(H_2PO_4)_3$ over a long time. $FeH_6(PO_4)_3$, on standing in a desiccator with P_2O_5, is transformed into the B form of $Fe(H_2PO_4)_3$, beginning on the third day and almost completely within two weeks. It is of interest that the A form of $Fe(H_2PO_4)_3$ is transformed into amorphous iron phosphate or $FeH_6(PO_4)_3$ with moisture absorption, and by dehydration of $FeH_6(PO_4)_3$ in a desiccator with P_2O_5 or silica gel, the B form and not the A form of $Fe(H_2PO_4)_3$ is directly obtained. From these facts, it is suggested that changes in the structures of the A and B forms of $Fe(H_2PO_4)_3$ caused by moisture absorption are completely different from each other.

From the results shown in Fig. 6, it is suggested that $FeH_6(PO_4)_3$ may contain more water than the A and B forms of $Fe(H_2PO_4)_3$. Based on the reversible change between $FeH_6(PO_4)_3$ and $Fe(H_2PO_4)_3$ structures caused by moisture absorption, it may be more reasonable to regard $FeH_6(PO_4)_3$ as another form of $Fe(H_2PO_4)_3$ since the A and B forms of $Fe(H_2PO_4)_3$ are isomorphous with the A and B forms of $Al(H_2PO_4)_3$, respectively. The existence of the C and D forms of $Al(H_2PO_4)_3$ other than the A and B forms has been reported,[11] while the C and D forms of $Fe(H_2PO_4)_3$, isomorphous with those of $Al(H_2PO_4)_3$, are unknown. Consequently, $FeH_6(PO_4)_3$ may be tentatively assigned the E form of $Fe(H_2PO_4)_3$. The experimental results are summarized schematically as follows:

$$\begin{tikzcd}
 & Fe(H_2PO_4)_3\text{ A form} \arrow[d, "\text{wet air}"] & \\
FeH_6(PO_4)_3 \arrow[dr, bend right, "P_2O_5"] & \text{amorphous iron phosphate} \arrow[l, "P_2O_5\text{ or silica gel}"'] \arrow[r, "\text{air}"] \arrow[d, shift left, "P_2O_5"] & FeH_3(PO_4)_2\cdot 2.5H_2O \\
 & Fe(H_2PO_4)_3\text{ B form} \arrow[u, shift left, "\text{wet air}"] \arrow[ul, bend left=60, "\text{air}"'] &
\end{tikzcd}$$

Amorphous iron phosphate obtained from the A and B forms of $Fe(H_2PO_4)_3$ and $FeH_6(PO_4)_3$ by moisture absorption gave crystalline $FeH_3(PO_4)_2\cdot 2.5H_2O$ on standing in air over 20 days. This product may be formed by the hydrolysis of amorphous iron phosphate.

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